Standard Operating Procedure
Determination of Trace Elements In Waters and Wastewaters by Inductively Coupled Plasma-Mass Spectrometry EPA Method 200.8

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1.0 Scope and Application

1.1 This method is applicable for the determination of dissolved and total recoverable metal analytes in ground water, surface water, wastewater and drinking water and describes the procedure for multi-element determination of trace metal elements by ICP-MS. This method is applicable to the following elements:

Element	Symbol	Isotopes Monitored	Isotope Used for Analytical Determination
Aluminum	Al	27	27
Antimony	Sb	121, 123	123
Arsenic	As	75	75
Barium	Ba	135, 137	137
Beryllium	Be	9	9
Cadmium	Cd	106, 108, 111, 114	111
Chromium	Cr	52, 53	52
Cobalt	Co	59	59
Copper	Cu	63, 65	63
Lead	Pb	206, 207, 208	206, 207, 208
Manganese	Mn	55	55
Molybdenum	Mo	95, 97, 98	98
Nickel	Ni	60, 62	60
Selenium	Se	77, 82	82
Silver	Ag	107, 109	107
Strontium	Sr	88	88
Thallium	Tl	203, 205	205
Uranium	U	238	238
Vanadium	V	51	51
Zinc	Zn	66, 67, 68	66

1.2 Dissolved elements are determined after the sample has been filtered and acid preserved. The dissolved solids should not exceed 0.2% (w/v) to avoid potential interferences.

1.3 For the determination of total recoverable analytes in aqueous samples a digestion is required before the analysis. Sample matrices that require digestion are aqueous samples that may contain particulate matter and/or suspended solids. If the particulate matter or the suspended solids in an aqueous sample exceeds 1% (w/v), then the sample must be digested as though it were a solid sample.

1.4 With the exception of Silver (Ag), where this method is approved for determination of certain metals and metalloid contaminants in drinking water, samples may be analyzed by direct analysis. The samples must be properly preserved with acid and have a turbidity of less than 1 NTU at the time of analysis.

1.5 Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Low recoveries of silver may occur in samples, fortified sample matrices and fortified laboratory blanks if determined as dissolved analytes or by direct analysis. Therefore, it may be necessary to digest samples before analyzing for silver. The acid digestion procedure used for total recoverable metals is employed for aqueous samples containing concentrations of up to 0.1 mg/L silver. Aqueous samples, which contain higher silver concentrations, should be diluted.

1.6 In the presence of free sulfate, the digestion procedure does not effectively solubilize barium. Analysis for barium should be completed as soon after sample preparation as is possible.

2.0 Summary of Method

This method is a multi-element determination of trace elements by ICP-MS in aqueous sample matrices. An aliquot of a well-mixed, homogeneous aqueous sample, whether total recoverable, dissolved or direct analysis, is accurately measured for sample processing. In all cases the water samples are prepared for analysis by addition of the appropriate amount of nitric acid. The sample is introduced by pneumatic nebulization into an inductively coupled argon plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and are separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer. A dynode electron multiplier detector detects the ions transmitted through the quadrupole and the ion information is processed by the data handling system. Isobaric elemental and polyatomic ion interferences must be recognized. All data obtained must be corrected for these types of interferences. See Section 4.

3.0 Definitions

3.1 Direct Analysis – The sample is analyzed without pre-analysis preparation such as filtration or digestion. Direct analysis is usually associated with acid preserved drinking water samples with turbidities of <1 NTU.

3.2 Dissolved Analytes – The concentration of analytes in an aqueous sample that will pass through a 0.45 μm membrane filter assembly prior to sample acidification.

3.3 Total Recoverable Analytes – The concentration of analytes determined either by direct analysis of an unfiltered acid preserved drinking water sample with turbidity of < 1 NTU, or by analysis of an unfiltered aqueous sample following the appropriate digestion procedure.

3.4 Reporting Limit (RL) – The lowest concentration of an analyte that can be determined quantitatively.

3.5 Linear Dynamic Range (LDR) – The concentration over which the instrument response to an analyte is linear.

3.6 Stock Standard Solutions for Calibration, Quality Control and Internal Standard – Concentrated solutions containing one or more of the method analytes prepared in the laboratory from assayed reference material or purchased from a commercial source. Calibration and standards used for quality control purposes should be obtained from two separate sources.

3.7 Tuning and Cross Calibration Solutions – A solution composed of specific analytes that is used for tuning, optimization and/or calibration of instrument components prior to the analytical procedure.

3.8 Calibration Blank and Continuing Calibration Blank (CCB) – A volume of reagent water acidified with the same acid matrix as the calibration standards. The calibration blank is also evaluated as the zero standard within the calibration curve and periodically throughout the analysis to verify baseline stability.

3.9 Calibration Standards – Solutions prepared by the dilution of stock standards in which the concentration of each analyte is known. The calibration standards are used to calibrate the instrument response with respect to analyte concentration.

3.10 Continuing Calibration Verification Standard (CCV) – A solution prepared from the appropriate stock standard that is monitored periodically throughout the analysis to verify that the instrument is properly calibrated.

3.11 Internal Standard – A solution which contains pure analytes, added to a sample, extract, or standard solution in known amounts. The internal standard is used to measure the relative responses of other method analytes that are components of the same sample or solution. All analytes used for the internal standard must not be present in any of the samples or standard solutions.

3.12 Laboratory Reagent Blank (LRB) - An aliquot of reagent water or other blank matrices that are treated exactly as a sample, including exposure to all glassware, plastic ware, equipment, solvents, and reagents. The laboratory reagent blank is used to determine if method analytes or other interferences are present in the laboratory environment.

3.13 Field Reagent Blank (FRB) - An aliquot of reagent water or other blank matrices that is placed in a sample container and treated as a sample in all respects, including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field reagent blank is to determine if method analytes or other interferences are present in the field environment.

3.14 Laboratory Control Sample (LCS) – A solution of method analytes of known concentration. The quality control sample is obtained from a source different than that used for the calibration stock standard solutions.

3.15 Laboratory Fortified Blank (LFB) – An aliquot of laboratory reagent blank to which a known amount of the method analytes are added in the laboratory. The laboratory fortified blank is analyzed exactly like a sample. The purpose of the LFB is to assess accuracy and precision and to determine whether the methodology is within accepted control limits

3.16 Laboratory Fortified Matrix (LFM) and Laboratory Fortified Matrix Duplicate (LFMD) – Two aliquots of the same sample to which known quantities of the method analytes are added in the laboratory, yet analyzed separately, with identical procedures. The laboratory fortified matrix (LFM) is used to assess whether the sample matrix contributes bias to the analytical results. The background concentrations of the method analytes in the sample matrix must be determined using a separate aliquot and the determined concentration values in the LFM must be corrected for the background concentrations. A minimum of 10% of the samples must be designated and fortified as LFM's. The LFMD, an aliquot of the same sample as that used for the LFM, and is used as an indicator of the precision of the laboratory procedure. Only one LFMD is required per batch.

3.17 Preparation Batch: A group of samples including quality control samples, which are processed together using the same method, the same lots of reagents, and at the same time or in continuous, sequential time periods. Samples in each batch should be of similar composition and share internal quality control standards.

3.18 Analytical Batch: A group of samples, including quality control samples, which are processed together using the same method, the same lots of reagents, and at the same time or in continuous, sequential time periods. Samples in each batch should be of similar composition and share common internal quality control standards.

4.0 Interferences

In the determination of trace elements by ICP-MS, there are five types of interferences that may contribute to inaccurate results. These are:

4.1 *Isobaric elemental interferences* occur when isotopes of different elements form singly or doubly charged ions of the same nominal mass-to-charge ratio that cannot be resolved by the mass spectrometer. Only molybdenum-98 and selenium-82 have isobaric elemental interference from krypton. This interference can be diminished by using high purity krypton free argon. If alternative analytical isotopes having higher natural abundance are selected all data obtained under these conditions must be corrected by measuring the signal from the isotope of the element which caused the interference, and subtracting the appropriate signal ratio from the isotope of interest. All correction equations used should be documented.

4.2 *Abundance sensitivity:* Defines the degree to which the wings of a mass peak contribute to the adjacent masses. The ion energy and quadrapole operating pressure affects the abundance sensitivity. Wing overlap interferences may occur when a small ion peak is being measured next to a large one. The instrument ion energy and operating pressure, along with spectrometer resolution, can be adjusted to minimize these interferences.

4.3 *Isobaric polyatomic interferences*. Are caused by ions consisting of more than one atom which have the same nominal mass-to-charge ratio as the isotope of interest and cannot be resolved by the mass spectrometer. These ions are formed in the plasma or interface region of the instrument from sample components and/or support gases. These are also listed under the "Molecule" section of the instrument control operating software. Appropriate correction equations used must be documented. These interferences are highly dependent on sample matrix and instrument conditions.

4.4 *Physical interferences* are associated with the physical processes that govern the transport of sample into the plasma, sample conversion processes in the plasma, and the transmission of the ions through the plasma-mass spectrometer interface. These interferences result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur during the transfer of a solution into the nebulizer due to a differing viscosity, at the point of aerosol formation and transport to the plasma because of surface tension, or during the excitation and ionization processes within the plasma. High levels of dissolved solids in the sample may contribute to deposits of material on the extraction and/or the skimmer cones reducing the orifice diameter and therefore decreasing the transmission of ions. Samples should not be introduced into the ICP-MS which contain dissolved solids greater than 0.2% (w/v) in order to reduce this effect. The use of internal standards can be effectively used to compensate and monitor for physical interference effects. Internal standards should be chosen so that they behave in the same manner as method analytes; finally *memory interferences* result when isotopes of elements in a previous sample contribute to the signals being measured in the next sample. Memory effects can result from excess sample being deposited on the skimmer and sampler cones, build-up of sample in the spray chamber, and build-up of sample material in the plasma torch. The actual site where these effects occur is dependent on the element. Flushing with a rinse blank between each sample can minimize these effects. The

possibility of memory effects should be recognized and suitable rinse times should be established. If memory interference is suspected the sample or samples should be analyzed again after a long rinse period.

5.0 Safety

5.1 All laboratory work is performed in accordance with the DHHS Public Health Environmental Laboratory (DHHS PHEL) Chemical Hygiene Plan.

5.2 Safety Data Sheets (SDS) can be found on the DHHS PHEL Share Drive (I:). The SDS should be read prior to handling chemicals or gases in the laboratory.

5.3 Protective clothing, such as lab coats, safety glasses, and gloves should be worn for protection when working with hazardous chemicals.

5.4 Acid resistant aprons and gloves should be used when handling concentrated acids. All laboratory safety protocols for acid handling should be followed. Small quantities (less than 250 mL) of concentrated acid may be kept on the laboratory bench in a dedicated concentrated acid container. Small quantities of concentrated acid (less than 50 mL) may be transferred or pipetted from this container in the laboratory environment.

5.5 Acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Environmental sample acidification should be done in a fume hood.

5.6 Instrument Safety

5.6.1 The overhead vent must be on at all times during this analysis.

5.6.2 The drain tubing leading to the waste container should not be cracked or brittle. The waste container should be emptied and the contents disposed of properly. See Section 16.0

5.6.3 The ICP-MS is fully interlocked to protect the user from dangers such as high voltages, radio frequency generators, and intense ultra-violet light. Under no circumstances should the operator attempt to disable these interlocks. Nor should the ICP-MS be operated if any safety interlock is known to be disabled or malfunctioning.

5.6.3.1 For a thorough discussion of the instrument safety consult the ICP-MS Manual.

6.0 Equipment and Supplies

6.1 Thermo Fisher Scientific iCAP Q ICP-MS. System capable of scanning the mass range of 5 – 250amu with a minimum resolution capability of 1amu peak width at 5% peak height and equipped with a dynode electron multiplier detector and other required peripherals such as recirculating pump, cones, etc.

6.2 ESI prepFAST SC4-DX Auto-sampler.

6.3 Peristaltic pump tubing

6.4 Membrane filtration apparatus

6.5 Microwave digestion system

6.6 Standard laboratory equipment including graduated cylinders, volumetric flasks, polypropylene screw cap tubes, pipettes, pipette tips and pH strips.

6.7 Type 1 water deionization unit, EMD Millipore DIRECT-Q3 UV or equivalent

6.8 Turbidimeter

7.0 Reagents and Standards

7.1 All reagents and standards are labeled and stored in accordance with the DHHS PHEL Chemical Hygiene Plan.

7.2 All standards used to prepare the calibration standards and quality control samples are entered into the Horizon LIMS Standards Log. See Section F of the Horizon 12.8 Orientation Guide for LIMS procedures concerning this standards log. However, Horizon is not a logbook for reagents and standards. These must be maintained in a logbook or recorded on the data packets. Horizon LIMS will not allow you to post any data obtained from expired QCs, standards or spiked samples. Horizon does not keep historical standards information.

7.3 All stock and working acids and reagents, along with all secondary and working standard solutions expire upon date set by manufacturer.

7.4 All working reagent solutions expire upon discoloration or expiration of stock, whichever is sooner. All secondary or working solutions are monitored for stability and replaced as needed or upon expiration of stock standards, whichever is sooner.

7.5 Deionized water (ASTM Type 1 water)

7.6 Tuning Solution at 1ppb for Ba, Bi, Ce, Co, In, Li and U. Commercially prepared.

7.7 Cross Calibration Multi Element Solution. Commercially prepared.

7.8 Multi Element Internal Standard Solution: *Concentration - 100 µg/ml*.

7.9 Multi-element Standard A: Contains Al, As, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Th, Tl, U. V and Zn. *Concentration - 10 mg/L.*

7.10 Multi-element Standard B: Contains Ag and Ba. *Concentration - 10µg/mL*.

7.11 Single element standards. Commercially prepared. *Concentration – 1000 µg/ml*

7.12 Nitric Acid (concentrated) Trace Metals Grade

7.12.1 Nitric acid (50% V/V): Add 500 mL concentrated HNO_3 to 400 mL deionized water and dilute to 1 L.

7.12.2 Nitric Acid (10% V/V): Add 100 mL concentrated HNO_3 to 800 mL deionized water and dilute to 1 L.

7.12.3 Nitric Acid (2% V/V): Add 20 mL concentrated HNO_3 to 800 mL deionized water and dilute to 1 L.

7.12.4 Nitric Acid (1% V/V) Add 10 mL concentrated HNO_3 to 800 mL deionized water and dilute to 1 L.

7.13 Hydrochloric Acid (concentrated) Trace Metal Grade

7.14 **Calibration Blank and Continuing Calibration Blank**

7.14.1 In a 50 mL plastic screw cap tube, pipette 1000 µL of 50% HNO_3 and bring to volume with deionized water. Mix thoroughly.

7.15 **Single and Multi -Element Stock Standard Solutions:**

7.15.1 Primary Calibration Stock Standards: All single elements – *1000 µg/mL*

7.15.1.1 **Secondary Calibration Stock Standard Solution**:

Final concentration is 10 mg/L.

In a 50 mL plastic screw cap tube containing 1000 µL of 50% HNO_3 and 25 mL of deionized water, pipette 500 µL of each of the single element stock standard solutions required for analysis. Dilute to volume with deionized water and mix thoroughly.

7.15.1.2 **Reporting Limit Calibration Stock Standard Solution**:
Final Concentration for Sb, Ba, Be, Cd, Cr, Co, Pb, Mn, Mo, Ni, Ag, Tl, U and V – 1 mg/L
Final Concentration for As, Sr - 2 mg/L
Final Concentration for Al - 4 mg/L
Final Concentration for Cu, Se and Zn – 5 mg/L
In a 50 mL plastic screw cap tube containing 1000 µL of 50% HNO_3 and 25 mL of deionized water, pipette 50 µL each of Sb, Ba, Be, Cd, Cr, Co, Pb, Mn, Mo, Ni, Ag, Tl, U and V; 100 µL each of As and Sr; 200 µL of Al and 250 µL each of Cu, Se and Zn. Dilute to volume with deionized water and mix thoroughly. Instrument auto-dilutor will do a 2x dilution on this standard to create and analyze Calibration Level 1.

7.15.1.3 **Working Calibration Stock Standard:**
Final Concentration is 100 µg/L for all elements.
In a 50 mL plastic screw cap tube containing 1000 µL of 50% HNO_3 and 25 mL of deionized water, pipette 500 µL of the secondary calibration stock standard in 7.15.1.1. Dilute to volume with deionized water and mix thoroughly. This standard is designated Calibration Level 6. The instrument auto-dilutor will do a 2x, 5x, and 10x dilution on this standard to create Calibration Level Standards 3, 4 and 5 at concentrations of 10, 20, and 50 µg/L respectively.

7.15.2 **Primary Continuing Calibration Verification (CCV) Standards:**
Obtain from a source different than that of the calibration standards.

7.15.2.1 Multi-element Standard A: *Concentration – 10 µg/mL*

7.15.2.2 Multi-element Standard B: Ba, Ag *Concentration – 10 µg/mL*

7.15.2.3 Strontium: *Concentration – 1000 µg/mL*

7.15.2.3.1 Secondary Strontium Standard:
Final Concentration - 10 mg/L
In a 50 mL screw cap tube containing 1000 µL of 50% HNO_3 and 25 mL of deionized water, pipette 500 µL of the Primary Strontium Standard. Dilute to volume with deionized water and mix thoroughly.

7.15.2.4 Working Continuing Calibration Verification (CCV) Standard:
Final Concentration - 50 µg/L
In a 50 mL plastic screw cap tube containing 1000 µL of 50% HNO_3 and 25 mL of deionized water, pipette 250 µL of both Primary Multi-element Standard A, Primary Multi-element Standard B along with 250 µL of the Strontium Secondary Standard. Dilute to volume with deionized water and mix thoroughly.

7.15.3 **Primary Laboratory Control Standard (LCS)** - Obtain from a source different than that of the calibration standards.

7.15.3.1 Multi-element Standard A: *Concentration – 10 µg/mL*

7.15.3.2 Multi-element Standard B: Ba, Ag *Concentration - 10 µg/mL*

7.15.3.3 Strontium: Concentration – 1000 µg/mL

7.15.3.3.1 Secondary Strontium Standard
Final Concentration - 10 mg/L

In a 50 mL plastic screw cap tube containing 1000 µL of 50% HNO_3 and 25 mL of deionized water, pipette 500 µL of the Primary Strontium Standard. Dilute to volume with deionized water and mix thoroughly.

7.15.3.4 Working Laboratory Control Standard (LCS):
Final Concentration – 20 mg/L
In a 50 mL plastic screw cap tube containing 1000 µL of 50% HNO_3 and 25 mL of deionized water pipette 100 µL each of Multi-element Standard A, Primary Multi-element Standard B along with 100 µL of the Secondary Strontium Standard. Dilute to volume with deionized water and mix thoroughly.

7.16 **Internal Standard Primary Stock Solution**:
Li^{+6}, Y, In, Ga, Sc, Tb, and Bi: Concentration 100 mg/L, along with Ge: Concentration - 1000 mg/L

7.16.1 Secondary Internal Standard Stock Solution: *Final Concentration - 5mg/L*
In a 50 mL plastic screw cap tube containing 1000 µL of 50% HNO_3 and 25 mL of deionized water, pipette 2.5 mL of the Multi-element Primary Stock Standard along with 250µL of the Primary Germanium Stock Standard. Dilute to volume with deionized water and mix thoroughly.

7.16.1.1 Working Internal Standard Solution:
Final Concentration - 5 µg/L
In a 100 0mL plastic volumetric flask containing approximately 500 mL of 1% HNO_3, pipette 1000 µL of the Secondary Internal Standard Stock Solution. Dilute to volume with deionized water and mix thoroughly. Transfer to the appropriate vessel on the auto-sampler cart.

7.17 **Primary Laboratory Fortified Matrix (LFM) and Laboratory Fortified Matrix Duplicate (LFMD)**

7.17.1 Multi-element Standard A: *Concentration – 10 µg/mL*

7.17.2 Multi-element Standard B: Ba, Ag *Concentration - 10 µg/mL*

7.17.3 Strontium: (1000µg/mL)

7.17.3.1 Strontium Secondary Standard: *Final Concentration – 10 mg/L*
In a 50 mL plastic screw cap tube containing 1000 µL of 50% HNO_3 and 25 mL of deionized water, pipette 500 µL of the Primary Strontium Standard. Dilute to volume with deionized water and mix thoroughly.

7.17.4 For direct analysis samples: *Final concentration - 50 µg/L for each element*
Into a 15 mL plastic screw cap tube containing approximately 10 mL of the chosen sample, pipette 75 µL each of the Primary Multi-element Standard A and Multi-element Standard B, along with 75 µL of the Secondary Strontium Standard. Dilute to volume with the appropriate sample and mix thoroughly.

7.18 For total recoverable analytes using microwave digestion: Reference current version of DHHS PHEL SOP 2170.1 for preparation of blank, calibration and quality control solutions.

7.19 For dissolved analytes filtered in the laboratory or field: Reference current version of DHHS PHEL SOP 2180.1 for preparation of blanks (both laboratory and field blanks), calibration and quality control solutions.

8.0 Sample Collection, Preservation, Storage and LIMS Login

8.1 Sample requests and login are performed according to DHHS PHEL SOP 1800.1 LIMS Login and Reporting and No. 1900.1 Customer Service Procedures.

8.2 Before the collection of an aqueous sample, the data user must determine the type of data required, which will determine the appropriate preservation and treatment steps necessary for the analysis.

8.3 For the determination of dissolved analytes, whether filtered in the laboratory or field, reference current version of DHHS PHEL SOP 2180.1 for sample collection and preservation requirements.

8.4 For the determination of total recoverable analytes in aqueous samples, reference DHHS PHEL SOP 2170.1 for sample collection and preservation requirements.

8.5 For the direct analysis of total recoverable analytes in drinking water, the samples are collected in various sized plastic containers depending upon the analytes to be determined.

8.6 The containers and volume required for acidification are listed below:

Plastic Container Size	Volume of 50% HNO3 required
1000 mL	20 mL
500 mL	10 mL
250 mL	5 mL
125 mL	2.5 mL

8.7 Samples should be returned to the laboratory within two weeks of collection and preserved upon receipt by laboratory personnel. Samples not preserved in this time frame will be rejected. Drinking water samples are preserved upon arrival at the laboratory using the appropriate volume of 50% nitric acid required for sample size, and allowed to stand for 16 hours before analysis may be performed. If necessary, additional acid may be added to bring the pH to < 2. Aqueous environmental samples are preserved in the field.

8.8 See DHHS PHEL SOP 6600.2 and Attachment 2 of this SOP for the turbidity determination procedure. If the sample turbidity is <1 NTU, the analytes may be determined using the direct analysis procedure. If the turbidity of the sample is >1 NTU, then the sample must be digested and reported as a total recoverable analyte analysis. Samples for public water systems that are >1 NTU are rejected and must be recollected.

8.9 If properly acidified, the samples can be held for up to six months before analysis.

9.0 Quality Control and Data Assessment

9.1 The quality control requirements of the DHHS PHEL Quality Assurance Plan (QAP) must be followed at all times.

9.2 The quality control program for this method includes the following: Initial Demonstration of Capability (IDC), continuing instrument performance checks, and assessment of data quality.

9.3 Initial demonstration of capability (IDC) is used to assess instrument and laboratory performance. The IDC consists of three parts: 1) establishing the linear

dynamic range (LDR) for each analyte; 2) analysis of a LCS and 3) the determination of the MDL for each analyte.

9.3.1 The detector primarily limits the linear dynamic range (LDR) of an analyte. However, the current ICP-MS instrument is equipped with an intelligent dilution program that dilutes any sample whose results are outside the calibration range, thereby eliminating the need to establish a broad LDR. Therefore, a LDR of 1000 µg/L has been established for all elements. An LDR should be determined whenever a significant change has been made to the system, including installation of a new detector or changes in the nebulizer or spray chamber type.

9.3.2 Laboratory control samples (LCS) must be successfully analyzed using the analytical method before beginning routine analysis. The LCS sample should be analyzed at both the beginning and end of the analytical run and acceptance limits of the LCS must be within 90 – 110 % of the true value of the standard.

9.3.3 MDL studies are done in accordance with EPA 200.8, DHHS PHEL SOP# 8200.1, the NPHEL Quality Assurance Plan and EPA's Definition and Procedure for the Determination of the Method Detection Limit, Revision 2 (Dec 2016). Replacement of a detector is cause for a new MDL study.

9.4 Laboratory performance assessment

9.4.1 Calibration Curve Acceptance Criteria: For all analyses, the resulting calibration curve must have a correlation coefficient greater than 0.995.

9.4.2 Continuing Calibration Blank (CCB) Acceptance Criteria: For all analyses, the baseline stability of the instrument must be verified on a continuing basis by the periodic analysis of a calibration blank (CCB). The CCB is analyzed after the calibration curve, after every ten (10) samples, and at the end of the sample run. The CCB must be less than the established reporting limit for the elements being analyzed.

9.4.3 Continuing Calibration Verification (CCV) Acceptance Criteria:
For all analyses, the calibration curve is verified on a continuing basis by the periodic analysis of a CCV. The CCV is analyzed after the calibration curve, after every ten (10) samples, and at the end of the sample run. The acceptance limit of the CCV is 90 – 110% of the true value. If the CCV determined value is not acceptable, then the instrument must be recalibrated and all samples since the last acceptable quality control assessment sample (QCAS) must be analyzed again.

9.4.4 Laboratory Control Sample Acceptance Criteria:
The accuracy of the calibration curve should be validated by the analysis of a LCS or external control. The LCS should be analyzed at the beginning and the end of each analysis. The determined value of the LCS must be within 90 - 110% of the true value.

9.4.5 Laboratory fortified matrix sample (LFM) Acceptance Criteria:
The analyte percent recovery is calculated using the following equation:

$$\text{Percent Recovery} = ((C_s - C) \div CA) \times 100$$

Where: C_s = Fortified sample determined concentration
C = Sample determined concentration
CA = Concentration of analyte added to fortify the sample

The percent recovery must be between 70 - 130% for all analytes. If the percent recovery is not within this range, then another sample may be chosen and spiked and analyzed within the same run. If reanalysis does not occur within the same run, all samples associated with this LFM must be prepared again and reanalyzed.

9.4.6 Laboratory fortified matrix duplicate (LFMD) Acceptance Criteria:
The laboratory performs one duplicate analysis per analytical batch using the same sample as that used for the LFM. Two criteria are required for acceptance of LFMD results: First, the percent recovery must be between 70-130% for all analytes. The analyte percent recovery for the LFMD is calculated using the following equation:

$$\text{Percent Recovery} = ((C_s - C) \div CA) \times 100$$

Where: C_s = Fortified sample determined concentration
C = Sample determined concentration
CA = Concentration of analyte added to fortify the sample

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Secondly, the relative percent difference (RPD) between the LFM and LFMD must be less than or equal to 20%. The relative percent difference is calculated using the following equation:

$$RPD = [(\,|\,C_{LFM} - C_{LFMD}\,|\,) \div [\,(C_{LFM} + C_{LFMD}) \div 2\,]\,] \times 100$$

Where: C_{LFM} = Determined concentration of LFM
C_{LFMD} = Determined concentration of duplicate LFM
$(C_{LFM-1} + C_{LFM-2}) \div 2$= Average of determined concentrations

If the RPD is greater than 20%, then the samples associated with that duplicate analysis should be prepared again and reanalyzed.

9.4.7 Internal Standard (IS) Response Acceptance Criteria: The internal standard response is monitored throughout the analysis. The ratios of the internal standards responses against each other also need to be monitored. This information can be used to detect potential problems caused by mass dependent drift, errors in the addition of the internal standards or increases in concentrations of individual internal standards caused by background contributions from the sample. The absolute response of any one internal standard must not deviate more than 60 - 125% of the original response in the calibration blank. If deviations greater than these are observed, instrument software will trigger a re-analysis of the sample utilizing a calculated dilution. Multiple dilutions may be analyzed until the internal standard response meets the established acceptance criteria. If the response criteria is not met within three attempts, the run will be suspended and a determination and preparation of a manual dilution should occur.

9.4.8 For total recoverable analytes using microwave digestion:
Refer to the current version of DHHS PHEL SOP 2170.1 for preparation of blanks, calibration standards and quality control solutions.

9.4.9 For dissolved analytes filtered in the laboratory or field: Refer to the

current version of DHHS PHEL SOP 2180.1 for preparation of blanks (both laboratory and field blanks), calibration standards and quality control solutions.

10.0 Calibration and standardization

10.1 The instrument should be tuned, optimized, and operated according to the manufacturer's recommendations.

10.2 Prior to the start of an analysis the Performance Report should be performed using the Performance Report Wizard available in the Instrument Control portion of the instrument software and using the Tune B solution. The performance evaluation must meet the sensitivity, stability and mass calibration tests established for the measurement mode required for analysis. If the specifications are not met, the Autotune procedure should be performed, followed by a repeat of the Performance Report. If this should fail, a Cross Calibration will need to be performed, using the cross calibration solution and followed by Autotune and a Performance Report.

10.3 Internal standardization must be used in all analytical determinations. The internal standards are used to compensate for instrument drift and physical interferences. The internal standard solution is added to all blanks, standards, and samples at identical levels using the syringe module on the autosampler and as designated in the method. Internal standards are selected in the Method Parameter portion of the lab book under "Analytes" and defined in the "Quantification" section. Once designated as an IS, the instrument software will automatically choose the isotope closest in mass to the analyte of interest, or the analyst may choose the "Interpolation" function. This is where a linear regression between two bracketing internal standards will correct the observed intensity of the analyte of interest.

11.0 Procedure

11.1 For total recoverable analytes using microwave digestion: Reference DHHS PHEL SOP 2170.1 for sample preparation procedure.

11.2 For dissolved analytes filtered in the laboratory or field: Reference DHHS PHEL SOP 2180.1 for sample preparation procedure.

11.3 The following procedure outlines analysis steps for total recoverable analytes (digested), dissolved analytes (filtered) or direct analysis total recoverable analytes:

- 11.3.1 For direct analysis samples determine sample turbidity (See Attachments 1 and 2).
- 11.3.2 Prior to analysis for all sample types, including total recoverable analytes (digested), dissolved analytes (filtered) or direct analysis analytes, appropriately label a 15mL plastic tube and fill with a well-mixed portion of sample.
- 11.3.3 Prepare all working calibration standards and quality control samples and place in the specified autosampler positions.
- 11.3.4 Prepare the appropriate number of LFM's and the LFMD (direct analysis total recoverable analytes).
- 11.3.5 Prior to analysis, prepare all autosampler reagents, fill the appropriately labelled containers, and properly empty the instrument waste container.

11.4 Sample analysis

11.4.1 Prior to igniting the plasma, turn on the chiller, autosampler and open both the "Instrument Control" and "Qtegra" portions of the instrument software. Tighten the peristaltic pump tubing and allow carrier solution to flow for several minutes through the nebulizer and spray chamber. Ignite the plasma and allow the instrument to warm up for a minimum of 20 minutes.

11.4.2 Perform the Performance Report procedure and check that all parameters are within specification. (Reference Section 10 for further information).

11.4.3 In "Instrument Control" initialize the autosampler, perform a dual rinse of the autosampler probe and load the "Prime" method. This method primes the syringes and tubing that connect the autosampler and instrument and prepares both for sample analyses. Press "GO" to run the Prime method. Once the "Prime" method is complete, close this method and load the appropriate method for sample analysis.

11.5 Instrument Set-up:

11.5.1 Dashboard: the Home Page of the instrument software opens to the "Dashboard" page, where you can view the instrument's operating status and configuration.

11.5.1.1 The "Get Ready" icon located at the top center of the dashboard must be green prior to analysis. Once the instrument is ready for use, simply click the icon to prepare the software for use.

11.5.2 Lab Book: located on the Home Page of the instrument software. All analytical measurements are managed through a Lab Book. A Lab Book allows the analyst to create and schedule analytical runs, evaluate results and export data. The Lab Book contains the method parameters, (including the unique laboratory batch number), sample list and data export options.

11.5.2.1 Lab Books can be created from a blank template, an existing Lab Book, or from an existing template. An existing template confers established method parameters on any analytical run created using the template, including sample definitions and defined actions for quality control requirements. Each Lab Book is given a unique designation, including date of analysis and requested elements. For further detailed instructions on the creation of the Lab Book, see the software operation manual. Once a Lab Book is created, it can be sent to the "Scheduler" queue for analysis. Once sent to "Scheduler," the Lab Book automatically starts. If multiple runs are scheduled, Lab Books will run in the order scheduled.

11.6 When the analysis is complete, insert carrier probe in a tube containing deionized water and allow the water to pump through for several minutes. During this rinse cycle, the auto-sampler probe should also be rinsed with deionized water by loading the appropriate method and allowing the uptake of the deionized water through the probe. When the rinse phase of clean-up is completed, remove the carrier solution probe from the container and allow the line to pump dry for a few minutes. From "Instrument Control," turn off the plasma. The instrument will go through the shut-down procedure. Loosen the tubes on the peristaltic pump. Move

the autosampler probe to its home position. Turn off the chiller and the autosampler.

12.0 **Data analysis, Calculations and Reporting**

12.1 All calculations necessary to convert raw data are performed by the instrument software. All calculations performed by the software are based on the ratio of the analyte intensity (cps) to the internal standard intensity (cps). In all calculations the ratio of analyte intensity to internal standard intensity is taken before any other is performed.

12.2 The software performs all calculations necessary for all QC samples. The values entered in the Standards section of Method Parameters in the software will determine the values used in the QC checking calculations.

12.3 Upon completion of the analysis, several functions become available in the Contents page of the Lab Book, including Query and Reports.

12.3.1 To view results for a completed Lab Book, open "Query" and create or choose the appropriate "Preset." The "Preset" allows you to create a query with the results required for the analysis by choosing from several parameters listed in the "Columns" and "Rows" menus. Once the Preset loads, results will be displayed in a spreadsheet format. The spreadsheet is saved to the appropriate folder on the "I" drive. Here, the results may be reformatted for export to the laboratory LIMS system.

12.3.2 Upon completion of the "Query" function, the data is now ready to be formatted for the final data packet. Click "Reports" and the Report View screen appears. Choose "Comprehensive" and click on "Display Report." Data will now be displayed as defined in the report format. Print.

12.4 All data, including the raw data spreadsheet, the data summary report, the standards and reagent tracking document, and the daily performance report are filed as part of the data packet. The data packet is labeled with the unique Horizon Batch Number (HBN), Department (MET) and batch number, and the dataset designation.

12.5 For each batch of samples one sample is calculated independently using an Excel spreadsheet. Reference Attachment 5 for this procedure.

12.6 Data is stored and archived according to procedures in DHHS PHEL SOP 1500.1

12.7 The results for samples and all applicable quality control samples are transferred to the Horizon LIMS system electronically. Reference Attachment 4 for a detailed discussion of the LIMS data transfer procedure.

12.8 Data and data qualifiers are entered according to DHHS PHEL SOPs 8320.1 and 1920.1. Appropriate comments regarding the quality of data are also written on the data packet. It is the responsibility of the analyst to do the first data review. The analyst should initial and date the data package upon completion of the batch review (BREV).

12.9 The second analyst must review the data and results for quality and accuracy before completion of the peer review (PREV) section in Horizon LIMS. Initial and date the data package. The entire packet is then scanned into Horizon and verified that it is in Horizon. Reference Attachment 6 for this procedure.

12.10 After completion of all analyst reviews, the entire data packet should be scanned into the Horizon LIMS system. See Attachment 4 for more information on this procedure.

12.11 The horizon system can generate quality control charts for various quality control sample types. To access control charts in LIMS, go to the "Data" tab, then "Charts", and then select or generate the appropriate control chart.

12.12 Samples that have an analyte concentration below the reporting limit are reported as <RL.

12.13 Samples which have an analyte concentration greater than the reporting limit, are reported to 3 significant figures.

12.14 Samples which have a lead concentration greater than the current action limit (15 µg/L) are reanalyzed for confirmation purposes. If the original result is confirmed the original result is reported. If the original result is not confirmed the sample is reanalyzed.

13.0 **Corrective Action and Maintenance**

13.1 Corrective Actions

13.1.1 Corrective actions for specific situations are discussed in detail throughout this document in the appropriate section.

13.1.2 Whenever instrument performance specifications are not met the necessary tuning and optimization should be performed in order to achieve performance specifications.

13.1.3 Whenever the results for any QC are not within the acceptable limits, the reason(s) should be determined and any necessary corrective action taken. Corrective actions should be documented in the raw data and noted in the data summary.

13.1.4 The QA or Lab manager should be notified of any unacceptable QC results, unusual sample results, or any situation in which the analyst suspects that the quality of the results or data has been compromised in any way.

13.1.5 Corrective action for both equipment and quality control problems will be documented according to DHHS PHEL SOP 8500.1

13.2 Maintenance

13.2.1 The Performance Report will be printed for each analytical run and placed with each data packet. Both are scanned into the laboratory LIMS system.

13.2.2 Pump oil is changed yearly during preventive maintenance visits.

13.2.3 Detailed instructions for maintenance of the spray chamber, nebulizer, torch, RF coils, sampler and skimmer cones is provided in the instrument manuals. Maintenance on these items should be done as is needed and recorded in the maintenance logbook.

13.2.4 All other maintenance performed on the instrument by the analyst or the instrument representative should be noted in the maintenance logbook, along with actions taken to correct any problems.

13.2.5 Preventive maintenance visits will be documented in the maintenance log book according to DHHS PHEL SOP 8200.1

14.0 **Method Performance**

Copies of annual MDL studies are available for review on the DHHS PHEL Share Drive (I:).

15.0 **Pollution prevention**

15.1 Dispose of all reagents, standards, and samples properly. Reference Section 16.
15.2 Care should be taken to eliminate the generation of intermediate standards. This also eliminates extra steps in the procedure and thus reduces the possibility of errors.

16.0 **Waste Management**

16.1 All laboratory waste will be managed according to the current version of DHHS PHE Laboratory Chemical Hygiene Plan. See SOP 7600.1.
16.1 All standards and samples which contain high concentrations of hazardous analytes should be disposed of in the metals hazardous waste container. Drain disposal after neutralization can be used for excess sample dilutions, preserved samples in storage tubes, acids, instrument waste and preserved samples.
16.2 Samples may be disposed of properly thirty days after results have been reported.

17.0 **References**

17.1 EPA Method 200.8, Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry, Revision 5.4 (1994).
17.2 Thermo Fisher Scientific, iCap Q Software Manual.
17.3 Thermo Fisher Scientific, iCap Q Operating Manual
17.2 Horizon 12.8 Orientation Guide 2019, Nebraska Public Health Environmental Laboratory, Horizon LIMS Training Manual

18.0 **Attachments**

18.1 Attachment 1 - Drinking Water Metals Preparation Procedure
18.2 Attachment 2 – Turbidity Calibration Procedure
18.3 Attachment 3 – Example of Standard and Reagent Tracking Record
18.4 Attachment 4 – Horizon LIMS Procedures
18.5 Attachment 5 – Independent Calculation Procedure
18.6 Attachment 6 – Document Scanning into Horizon

Attachment 1: Drinking Water Metals Preparation Procedure

Sample Acidification:

1. Upon receipt, all samples must be acidified as outlined in Section 8.5.
   Note: Samples must be allowed to stand for a minimum of 16 hours prior to the determination of pH and turbidity.
2. Mark each sample container with the date of acidification
3. Sort by analyte(s) requested and transfer the sample containers to the appropriate area on the storage cart.

Turbidity Determination:

1. Reference Attachment 2 for a detailed description of both the quarterly and daily turbidity calibration procedure.
2. On the "pH and Turbidity" record sheet, fill in all sample information, along with the vial rack number, analyst and date of determination.
3. For each sample, pour approximately 30 mL of liquid into a turbidity vial that corresponds to the same position and in the same order as written on the record sheet. At the same time, the sample may be prepared for instrument analysis by filling an appropriately labelled 15 mL screw cap tube with sample, which is then capped and placed in a color coded rack.
4. Check to determine that the pH is less than 2 using a pH indicator strip. If <2, place a checkmark in the appropriate column on the record sheet. If the pH is >2, add more acid to the sample, mix thoroughly, and allow the sample to stand for another 16 hours. Re-check the pH and re-pour the turbidity vial. If necessary, repeat this step until the pH has been verified to be < 2 for all samples. Cap the turbidity vials.
5. Perform the Daily Standards Verification as outlined in the instrument manual. Determine and record the turbidity for each sample. Any sample with a turbidity >1 NTU needs special consideration. Management will be notified when this occurs and provided with sample identification numbers. A determination will be made whether the sample is to be rejected, digested and analyzed, or analyzed without digestion and reported with a data qualifier.

Attachment 2 - Drinking Water Metals Turbidity Determination

HACH 2100AN Turbidimeter Calibration:

1. Turn the 2100AN on and allow it to warm up for 30 minutes. If the 2100AN is being used routinely, it should be left on 24 hours a day.
2. Check to make sure the instrument is on the following settings: **RANGE** = Automatic, **SIGNAL AVG** = on, **RATIO** = on, **UNITS/EXIT** = NTU
3. Gently tip the 20, 200, 1000, 4000, and 7500 Stablcal® Standards back and forth. Allow the Stablcal® Standards to sit for 5 minutes. The <0.1 NTU Stablcal® Standard should not be tipped or shaken.
4. Press the **CAL** button. The **CAL** mode lights and the small green **LED** digits in the mode display flashes 00.
5. Remove the <0.1 NTU Stablcal® Standard from the case.
6. Wipe the standard cell clean and apply a thin film of silicone oil.
7. Align the mark on the standard cell with the mark on the instrument cell holder. Place the standard cell into the instrument. Close the cover.
8. Press the **ENTER** button. The instrument display counts down from 60 to 0, and then makes a measurement. This result is stored and used to calculate a correction factor for measurement of all NTU Standards.
9. The instrument automatically goes to the next standard and the standard number 01 appears in the mode display.
10. Remove the 20 NTU Stablcal®Standard from the case.
11. Wipe the standard cell clean and apply a thin film of silicone oil.
12. Align the mark on the standard cell with the mark on the instrument cell holder. Place the standard cell into the instrument. Close the cover.
13. Press the **ENTER** button. The instrument display counts down from 60 to 0, and then makes a measurement. This instrument applies the correction factor for turbidity of the <0.1 NTU Stablcal®.
14. The instrument automatically goes to the next standard and the corresponding standard number appears in the mode display.
15. Repeat steps 10-14 with the 200, 1000, 4000, and 7500 NTU Stablcal® Standards.
16. Press the **CAL** button. The instrument calculates and stores the new calibration information. The instrument is then returned to the measurement mode.
17. To print the new calibration data, press the **CAL** button, and then the **PRINT** key. Press the **UNITS/EXIT** key to return to the measurement mode and save the calibration data.
18. The calibration procedure should be performed every 3 months.

HACH Turbidimeter Daily Procedure:

Calibration Standards Verification:

1. Turn the 2100AN on and allow it to warm up for 30 minutes. If the 2100AN is used routinely, it should be left on 24 hours a day.
2. Check to make sure the instrument is on the following settings: **RANGE** = Automatic, **SIGNAL AVG** = on, **RATIO** = on, **UNITS/EXIT** = NTU
3. Gently tip the 20, 200, 1000, 4000, and 7500 Stablcal® Standards back and forth. Allow the Stablcal® Standards to sit for 5 minutes. The <0.1 NTU Stablcal® Standard should not be tipped or shaken.
4. To print the current calibration data, press the **CAL** button, and then the **PRINT** key. Press the **UNITS/EXIT** key to return to the measurement mode.
5. Remove the <0.1 NTU Stablcal® Standard from the case.
6. Wipe the standard cell clean and apply a thin film of silicone oil.
7. Align the mark on the standard cell with the mark on the instrument cell holder. Place the standard cell into the instrument. Close the cover.
8. Allow the reading to stabilize. Record the reading on the Turbidity calibration verification log sheet. For all the Stablcal® Standards the determined value should be within ±10% of the true value for that standard. Press **PRINT**.
9. Repeat steps 5-8 for the 20, 200, 1000, 4000, and 7500 Stablcal® Standard

Calibration Verification:

10. Remove the stray light Gelex secondary standard from its box.
11. Wipe the secondary standard cell clean and apply a thin film of silicone oil.
12. Align the mark on the standard cell with the mark on the instrument cell holder. Place the secondary standard cell into the instrument. Close the cover. Allow the reading to stabilize. Record the reading on the Turbidity calibration verification log sheet. For all the Gelex Secondary Standards the determined value should be within ±10% of the determined value for that secondary standard. Press **PRINT**.
13. Repeat steps 10-12 for the remaining Gelex Secondary Standards, 0-2, 0-20, 0-200, 200-4000, and 4000-10000 NTU.

Sample Turbidity Determination

14. Remove the first sample turbidity vial or sample cell from the turbidity vial rack.
15. Wipe the sample cell clean and apply a thin film of silicone oil.
16. Align the mark on the sample cell with the mark on the instrument cell holder. Place the sample cell into the instrument. Close the cover. Allow the reading to stabilize. Record the reading on the pH and turbidity log sheet. Press **PRINT**.
17. Repeat steps 14-16 for the remaining sample turbidity vials.
18. Any sample with a turbidity of greater than 1 NTU needs special consideration. Report any samples >1 NTU to lab management.
19. Make a Horizon LIMS Batch Worklist for the Turbidity samples analyzed.
20. Post the turbidity results. The default value of < 1 NTU is reported if the sample meets the drinking water turbidity standard. The date of analysis is also posted with the results.

Attachment 3: Example of Standard and Reagent Tracking Record

ICP-MS Standards and Reagents Tracking Record

Analysis Date: MET Batch No.: HBN No.:

Stock Standard Solutions:

Single Element Stock Standards Information (Mfg. – Inorganic Ventures Exp. Date – 19May21)						
Element	**Concentration (µg/mL)**	Lot Number	**Date Received**	**Date Opened**	**TCT Expiration Date**	**Analyst**
U	1000					
Single Element Stock Standards Information (Mfg. - Perkin Elmer)						
Element (s)	**Concentration (µg/mL)**	Lot Number	**Date Received**	**Date Opened**	**Expiration Date**	**Analyst**
Al	1000					
Sb	1000					
As	1000					
Ba	1000					
Be	1000					
Cd	1000					
Cr	1000					
Co	1000					
Cu	1000					
Ge	1000					
Pb	1000					
Mn	1000					
Mo	1000					
Ni	1000					
Se	1000					
Sr	1000					
Ag	1000					
Tl	1000					
V	1000					
Zn	1000					
Single Element Stock Standards Information (Mfg. - LGC) (Stable Pak Exp. Date – 01Jul20)						
Element (s)	**Concentration (µg/mL)**	Lot Number	**Date Received**	**Date Opened**	**Expiration Date**	**Analyst**
Sr	1000					
Multi-Element Stock Standards Information (Mfg. - LGC)						
Element (s)	**Concentration**	Lot Number	**Date Received**	**Date Opened**	**Expiration Date**	**Analyst**
Li, Sc, Ga, Y, In, Tb, Bi	100 µg/mL					
Std. A: Al, Sb, As, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Tl, U, V, Zn	10 µg/mL					
Std. B: Ag, Ba	10 µg/mL					

Filtration and Digestion

For Multi-Element Custom Stock Standard for Digestion and Filtration (Mfg. - ESI)						
Element (s)	**Concentration**	Lot Number	**Date Received**	**Date Opened**	**Expiration Date**	**Analyst**
Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Ag, Sr, Tl, U, V, Zn	100 µg/mL					

Instrument Tuning Solutions

Tune B Solution (Mfg. TCT Exp. Date: 16Dec23)							
MFG.	**Element(s)**	**Concentration (µg/L)**	**Lot Number**	**Date Rec'd**	**Date Opened**	**Expiration Date**	**Analyst**
Inorganic Ventures	Ba, Bi, Ce, Co, In, Li, U	1					

Cross Calibration Solution (Mfg. Exp. Date: 08Feb21)							
MFG.	**Element(s)**	**Concentration (µg/L)**	**Lot Number**	**Date Rec'd**	**Date Opened**	**TCT Expiration Date**	**Analyst**
Inorganic Ventures	Be	35					
	Zn	20					
	Cu, Ni	15					
	Al, Ga, Mg	10					
	Co, Li, Sc	8					
	Ag, Mn	6					
	Sr	5					
	Ba, Tl	4					
	Bi, Ce, Cs, Ho, In, Rh, Ta, Tb, U, Y	3					

Reagents:

Nitric Acid (Mfg. – Fisher)					
Reagent	Date Prepared	Expiration Date	Lot Number	Concentration	**Reagent Expiration Date**
Auto Sampler Carrier Solution	06-17-2020				
Auto Sampler Rinse	06-25-2020				
Auto Sampler Probe Rinse	06-25-2020				
For Sample Acidification	01-15-2020				
For Standard Prep	01-15-2020				

Quality Control Sample Preparation:

Name of Quality Control Sample	Date Prepared	Prepared from:	**Expiration Date**
LFM		Multi-element Std. A, B and Sr Secondary Std.	
LFMD		Multi-element Std. A, B and Sr Secondary Std.	

Primary and Secondary Standard Information

Name of Standard Prepared	**Date Prepared**	**Prepared Using**	**Elements**	**Final Analyte Concentrations**	**Analyst**	**Expiration Date**
Secondary RL Calibration Standard		1000 µg/mL PE Single Element Stock Standard Solutions	Sb, Be, Cd, Cr, Co, Pb, Mn, Mo, Ni, Ag, Tl, U, V	1 mg/L		
			As, Sr	2 mg/L		
			Al Cu, Se, Ba, Zn Ag, Ba	5 mg/L		
Secondary Calibration Stock Standard		1000 µg/mL PE Single Element Stock Standard Solutions	Al, Sb, As, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Sr, Tl, V, Zn, Ba, Ag, U	10 mg/L		
Primary CCV and LCS Multi-element Standard A		10 µg/mL Stock Standard Solution	Al, Sb, As, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Tl, U, V, Zn	10 mg/L		
Primary CCV and LCS Multi-element Standard B		10 µg/mL Stock Standard Solution	Ag, Ba	10 mg/L		
Secondary CCV and LCS Strontium Standard.		1000 µg/mL LGC Stock Standard Solution	Sr	10 mg/L		
Secondary Internal Standard Solution		Int. Std. LGC Primary Stock Standard	Bi, In, Li, Tb, Y	5 mg/L		
		Germanium PE Single Element Stock Standard	Ge	5 mg/L		

Working Calibration, Quality Control and Internal Standards:

Name of Standard Prepared	Date Prepared	Prepared Using	Elements	Final Analyte Concentrations	Analyst	Expiration Date
Calibration Blank				0		
RL Calibration Standard		Secondary RL Calibration Standard	Sb, Be, Cd, Cr, Co, Pb, Mn, Mo, Ni, Ag, Tl, U, V	1 µg/L		
			As, Sr	2 µg/L		
			Al, Cu, Se, Ba, Zn	5 µg/L		
Calibration Std.		Secondary Multi-element Standard A and B and Secondary Sr Standard	Al, Sb, As, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Sr, Tl, V, Zn, Ba, Ag, U	100 µg/L		
LCS		Primary Multi-element Standard A and B and Secondary Sr Standard	Al, Sb, As, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Sr, Tl, V, Zn, Ba, Ag, U	20 µg/L		
CCV		Primary Multi-element Standard A and B and Secondary Sr Standard	Al, Sb, As, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Sr, Tl, V, Zn, Ba, Ag, U	50 µg/L		
Internal Standard		Secondary Internal Std. Solution	Bi, In, Li, Tb, Y	5 µg/L		
			Ge	5µg/L		

Attachment 4: Horizon LIMS Procedures for Metals Analysis

Note: if needed, reference Horizon 12.8 Orientation Guide 2019, Nebraska Public Health Environmental Laboratory, Horizon LIMS Training Manual for more detailed instructions.

1. **Creating a Horizon Batch**
   1.1. From the Home Page in Horizon, select the Metals Department.
   1.2. On the Backlog: Metals (MET) tab, several categories of analysis are listed. Click the category for EPA 200.8, Liquid, Analysis under the Batch Rule header to view the samples ready for analysis.
   1.3. Highlight all samples chosen for analysis and click on the "Create Batch" tab.
   1.4. Make any necessary adjustments to the batch, including the addition of any required quality control samples, click Save and print the Batch Worklist.

2. **Creating a Lab Book using Qtegra software:**
   2.1. Using the Qtegra portion of the iCAP software, create a Lab Book using an existing template or a previously created Lab Book. Each Lab Book is given a unique designation, which may include date of analysis, requested analytes and the Metals batch number. Select "Create Lab book" when ready.
   2.2. All necessary rows for analysis will appear, including lines for all quality control samples and calibration curve standards (if created from a template or previously created Lab book). Insert identification numbers for each sample slated for analysis. In the "Comment" column of the Lab Book, insert the Metals Batch Number. This is necessary for transfer of data to LIMS. SAVE and send to the "Scheduler" queue for analysis.

3. **Data Transfer:**
   3.1 Upon completion of the analysis, new options will appear in the Lab Book Content section which allows data to be transferred to LIMS.
   3.2. Click on "Query" – a "Result" screen will appear. From the drop down menu, select a HDX Preset that has been created for the type of analysis performed and click the recycle arrows, ↻, to the left of the drop down menu. This opens the results of the analysis in the format required for LIMS transfer. (*Note*: this specific format is critical for proper transfer of data. Columns should not be altered, except in the case when elements not analyzed in the analysis may be removed). Click the "Export" icon at the top of the page. An "Export Data" screen appears. Under the "Excel Export Options" section of the export data screen, navigate to the I:drive and open the ICap Exports folder and click "SAVE". The lab book and all results will now open in an Excel spreadsheet. Make any necessary corrections or changes and click on "File" "Save as" and under file type, select CSV (MS-DOS) (*.csv). Click on the HDXIN folder and click "SAVE".
   3.3. When the file disappears, data has been successfully transferred to LIMS and is ready for upload and initial review.
   3.4. All export files are archived in the following location: I:\ICap Exports\archive.

4. **Data Upload and Batch Review**
   4.2. Data Upload:
      4.2.1. On the Horizon Home Page, click on "Data" then "Results Upload." The "Data Pipeline" screen will appear.

4.1.1.1 On the “Filter” tab on the “Data Pipeline” screen, select the Metals queue and enter the Horizon Batch number. Click SAVE. All data associated with the selected batch will appear in the bottom half of the screen.

4.1.1.2 Review all data for accuracy and correct any problems encountered. Highlight all samples and click the “Upload Results” tab. All data will disappear. Batch is now ready for review

4.2 Data Review

4.2.1 From the Horizon Home Page, under “Samples,” select “Batches” and enter the Horizon Batch Number (HBN) and hit ENTER. The Batch will appear with all associated samples.

4.2.2 Select “Edit results” to view reported results for all samples, including quality control samples. Results may be reviewed in a variety of ways by clicking on the tabs in the Display header: the “by Sample” tab reviews each sample individually, whereas the “Results” tab allows a review of the complete batch as it was created. The “QC” tab allows for the review of all acceptance limits, including percent recoveries and relative percent differences (RPD).

4.2.2.1 Batch Review (BREV)

4.2.2.1.1 Once all results have been verified, batch is ready for approval. Select the “Complete Review” tab to complete this level of review. LIMS will designate that the batch is ready for Peer Review.

4.2.2.2 Peer Review (PREV)

4.2.2.1.2 Upon completion of the initial review, a second analyst reviews the data and results for accuracy and quality. When ready, select the “Complete Review” to finalize this step.

Attachment 5: Independent Calculation of Results

1. Access Excel spread sheet for independent calculation of results using the following pathway: I:\Metals\ICP-MS\ICP-MS Independent Calculations.xlxs.

2. Open the Sample Results tab. Enter the Lab ID, Analysis Date, Horizon Batch information, and the instrument determined results for each analyte. This information will be carried through automatically to each analyte page.

3. Open the Sc Group tab. Enter the Measured Mean Intensity (Analyte-Column B) for each of the calibration standards for the first analyte. Enter the Measured Mean Intensity for the Internal Standard (IS-Column C) associated with each of the calibration standards for the first analyte. The Measured Mean Intensity for the Internal Standard for each of the calibration standards will be carried through automatically for the other analytes in the Sc Group.

4. The sample information is entered on the line under the label Sample Dilution. Enter the dilution factor (Column A) for the sample. Enter the Measured Mean Intensity (Column B) for the first analyte in the sample. Enter the Measured Mean Intensity (Column C) for the Internal Standard in the sample. The Measured Mean Intensity for the Internal Standard in the sample will be carried through automatically for the other analytes in the Sc Group.

5. Using the equation $y = mx + b$, the analyte concentration for the first analyte in the Sc Group is calculated. The calculated value appears in Column G under the Conc. label.

6. Repeat steps 3-5 for each of the other analytes in the Sc group.

7. Repeat steps 3-6 for the Ge Group, In Group, and Tb Group.

8. Print the information from the Sample Results tab.

9. Print the information from the Sc Group, Ge Group, In Group, & Tb Group tabs.

10. The printed independent calculation results should be included in the data packet for that batch.

Attachment 6: **Document Scanning into Horizon**

1. Document scanning into Horizon begins at the copier/scanner where the scan function is selected. Select one of the following buttons based on the type of document being scanned: Attachments for attachment documents, Batch for batch documents, Chain for sample documents and InstReports for instrument report documents.

2. Once scanning is complete, the hcmfiles folder on the LABSHARE drive can be checked for the number of documents scanned and any error files. There are four folders in the hcmfiles folder – one for each of the four types of scan documents listed above (see section 1). Document count files and error files should be moved to the archive folder under each document type folder once they have been reviewed.

3. To view scanned documents in Horizon LIMS V12, Select **Data → Documents** from the menu at the top of the Horizon screen. You can filter the FileType column of the document list by sample number or batch number to limit the list to the documents scanned.

Standard Operating Procedure
Determination of Trace Elements In
Waters and Wastewaters
by
Inductively Coupled Plasma-Mass Spectrometry
EPA Method 200.8

DHHS PHE Laboratory SOP No. 2800.2A

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Public Health Environmental Laboratory

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Approved by: _____ Lab Manager Date: 7-7-20